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Guidance for BAT-Equivalent Control of Selected Toxic Pollutants

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16. ABSTRACT

This manual is intended to provide guidance to federal and state NPDES permit and pretreatment staffs in determining appropriate limitations for the discharge of selected toxic pollutants in the wastewater from industrial facilities where applicable Effluent Guidelines regulations are not available. From his extensive knowledge and comprehensive review of the treatment technology available to industry, the author has determined, in his best professional judgement, the final effluent concentrations that can be achieved using his estimate of best available technology (BAT) for the following toxic pollutants: arsenic, barium, cadmium, hexavalent chromium, total chromium, copper, cyanide, fluoride, iron, mercury, nickel, silver, and zinc. It is concluded that, aside from a few extraordinary situations involving unusual chemical interferences, the treatability levels provided in the manual should be applicable, independent of industrial category.

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GUIDANCE FOR BAT-EQUIVALENT CONTROL OF SELECTED TOXIC POLLUTANTS

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FOREWORD

As mandated by the Clean Water Act of 1977 and the Great Lakes Water Quality Agreement of 1978, control of toxicants being discharged to the Great Lakes Basin and elsewhere in Region V is a continuing concern of the U.S. Environmental Protection Agency and the State pollution control agencies. This manual is intended to provide guidance to federal and state NPDES permit and pretreatment staffs in determining appropriate limitations for the discharge of selected toxic pollutants in the wastewater from industrial facilities where applicable Effluent Guidelines regulations are not available.

Funding for this project was provided by the Great Lakes National Program Office as authorized under Section 104(b) of the Clean Water Act and as partial fulfillment of Article VI and Annex 12 of the Great Lakes Water Quality Agreement.

I. INTRODUCTION

Regulations for the control of point source industrial pollutants are predicated upon the performance achievable by in-plant control measures and/or end-of-pipe wastewater treatment technologies. For the fourteen pollutants considered in this report,

Arsenic	Copper	Mercury
Barium	Cyanide	Nickel
Cadmium	Fluoride	Silver
Chromium-Hexavalent	Iron	Zinc,
Chromium-Total		

end-of-pipe treatment technology performance is usually concentration limited.

For example, for precipitation/solids removal treatment of a metallic pollutant, performance in a well designed and properly operated treatment plant is constrained to that effluent quality achievable through the conversion (by precipitation) of the soluble metallic pollutant to a solid form, and the subsequent removal of that solid phase. Neither complete conversion of the soluble pollutant to a solid, nor total removal of that solid, is possible with existing wastewater treatment technologies. Thus, an end-of-pipe treatment technology-based effluent limitation must incorporate factors reflecting both the degree of conversion possible for soluble to solid phase, and the performance of the solids separation technology. Where in-plant control measures are applied, mass discharges of pollutants may be reduced even below that level achievable by end-of-pipe treatment alone.

In making the final BPJ/BAT determinations, consideration should be given to the reduction of wastewater volumes and/or raw waste loads that could decrease pollutant mass loadings to the environment. Such reductions might be achieved by wastewater recycling systems, production process modifications, or individual process waste stream pretreatment schemes.

Many different categories of industry discharge common pollutants, and utilize common treatment technologies in the control of these pollutants. The best foundation upon which to

develop technology based effluent limitations is the performance of well designed and properly operated treatment systems. In such systems, among different industries, comparable effluent concentrations are observed for identical pollutants. The exception to this situation occurs in instances of improperly designed or constructed, or inadequately operated systems, or where plant-unique characteristics of a wastewater interfere with the performance of the treatment technology.

In this latter instance, particular effort on in-plant control, or specialized treatment methods, may be required in order to achieve effluent quality comparable to other treatment systems. Typically, however, technology based effluent limitation values, in the absence of site-specific wastewater characteristics which interfere with treatment, should be uniform when expressed on a concentration basis (1). In fact, experience has shown, and the removal data confirm, that even when several of the cited pollutants are present in the same wastewater the BPT-equivalent and BAT-equivalent final concentrations for each still can be achieved by using treatment conditions intermediate between those optimum for each pollutant when treated alone. Several states, including California, Delaware, and Illinois, have successfully applied uniform industrial effluent standards for many years. These uniform standards have been enforced equally for all industrial categories within such states.

The objective of this report is to identify effluent concentrations and associated treatment technologies representing BPT-equivalent and BAT-equivalent end-of-pipe control of the fourteen pollutants cited above. The conclusions presented in this report are based upon the results of several studies on available wastewater treatment technologies and their associated levels of full-scale performance. The first study was initiated in 1970, in support of the development by the State of Illinois Pollution Control Board of uniform industrial effluent standards (2). The results of that original study were updated in 1973 (3) and again in 1974 (4). A new study was undertaken in 1976-77

on behalf of the State of Illinois, to develop a document on industrial pollution control which reflected the accomplishments of industry in complying with the Federal Water Pollution Control Act Amendments of 1972 (PL 92-500), which required that industry achieve "Best Practicable Control Technology Currently Available," or BPT, by 1977 (5). Concurrent with that effort, proposed and promulgated BPT mass-discharge guidelines were reviewed, and converted to concentrations to provide a common basis for comparison (6). A review of the results of this program was published in the professional literature in July, 1977, the date for BPT compliance set by PL 92-500 (1). Finally, during 1980-81, these studies have again been updated and a text is in preparation which reflects the full range of technical options and performance capabilities for over twenty industrial pollutants, including those considered in this report (7). Thus, while this report, by intent, is concise, the literature base underlying it is extensive and represents almost continuous evaluation of treatment technology performance data, beginning in 1970. Reference 5 in particular, which is available through the National Technical Information Service, provides a full technical documentation for the conclusions presented in this report.

The achievement of BAT-equivalent effluent quality, as cited in this report, requires concurrent stringent control of effluent suspended solids. For most existing treatment plants, this level of suspended solids control would necessitate the addition of a filtration device. New plants, if properly designed, constructed and operated, might achieve an equivalent effluent suspended solids level without filtration.

II. REVIEW OF BPT-EQUIVALENT CONTROL

During 1975 and 1976, a study was undertaken on behalf of the State of Illinois to review and evaluate the BPT standards proposed and promulgated by the USEPA (6). This evaluation revealed that there were major differences in the levels of pollution control performance proposed by the USEPA for like pollutants for different categories of industrial dischargers. These differences were observed for pollutants common to many industries, and occurred for pollutants generally controlled by similar types of treatment technology, irrespective of the industrial wastewater source. Tables 1 and 2 demonstrate these differences among industry categories and subcategories, for several example pollutants.

Under the requirements for BPT effluent limitations guidelines, the inorganic constituent arsenic is regulated for four industrial categories, two of which include multiple subcategories for which arsenic is regulated (Table 1). The minimum arsenic guideline (on a concentration basis) was 0.01 mg/l, for the phosphorus-consuming (phosphorus trichloride) subcategory of the Phosphate Manufacturing category. Highest effluent arsenic levels, at 10.0 mg/l, were allowed for two of the three subcategories of the Nonferrous Metals industry. The third subcategory, however, had an arsenic limitation of only 0.1 mg/l. For all categories for which arsenic was regulated, the range of limitations was 0.01 to 10 mg/l, a 1000-fold span. Within the Nonferrous Metals category alone, there was a 100-fold range of arsenic standards.

Table 1. BPT Effluent Limitations Guidelines for Arsenic (1).

Industry	Subcategory	Guideline, mg/l
Inorganic Chemicals	Boric Acid-Ore Mined Borax	0.5
Nonferrous Metals	Primary Copper Smelting	10.0
	Primary Copper Refining	10.0
	Primary Zinc	0.1
Ore Mining & Dressing	Ferroalloy Ores	0.5
	Uranium, Radium, Vanadium	0.5
Phosphate	Phosphorus Consuming	0.01

Similar anomalies were observed in the guidelines for other inorganic pollutants. Copper was regulated for six industrial categories encompassing 11 subcategories, and guideline concentrations ranged from 0.03 to 1.1 mg/l, a near 40-fold span. Although the guidelines were fairly consistent among subcategories of each category, one Nonferrous Metal subcategory had a low copper guideline of 0.03 mg/l, while three other subcategories had guidelines of 0.3 mg/l, a 10-fold difference.

Table 2 summarizes the high and low guideline values for nine inorganic pollutants. Arsenic and copper have been discussed. The data for the remaining seven pollutants demonstrate that BPT guideline variability was typical, for all pollutants listed in Table 2. The range of guideline values for total chromium is 100-fold, total cyanide and zinc are 50-fold, and others range down to 10-fold.

Table 2. Range of Thirty-Day Average BPT Values, mg/l (1).

Pollutant	Low Industry	Lowest Value	Highest Value	High Industry
Arsenic	Phosphate	0.01	10.0	Nonferrous Metals
Cadmium	Ore Mining & Dressing	0.05	0.50	Nonferrous Metals
Chromium(T)	Rubber Processing	0.05	5.0	Leather Tanning
Copper	Nonferrous Metals	0.03	1.1	Inorganic Chemicals
Cyanide(T)	Ore Mining & Dressing	0.01	0.5	Organic & Inorganic Chemicals
Fluoride	Phosphate	0.7	29.0	Glass
Lead	Rubber Processing	0.1	2.1	Inorganic Chemicals
Nickel	Ore Mining & Dressing	0.1	2.2	Inorganic Chemicals
Zinc	Ore Mining & Dressing	0.1	5.0	Nonferrous Metals

Since under PL 92-500 (and subsequent federal legislation, i.e., the Clean Water Act of 1977), BPT and other effluent limitations are technology-based, the spectrum of effluent limitations proposed by the USEPA was surprising. In order to further assess this situation, the State of Illinois established in late 1975 the Illinois Effluent Standards Advisory Group, IESAG. The charge to the IESAG included the following:

- To review the technical basis upon which Illinois Effluent Standards had been based ... ... (and such additional information as may be appropriate, in order to) ... adequately define the limits and economics of state-of-the-art (industrial) pollution abatement technology.
- To determine, to the extent that the state-of-the-art of wastewater treatment had advanced, what concentrations of effluent pollutants could be technologically achieved and at what costs.
- To assess the applicability of mass discharge standards as an alternative to, or in concert with Illinois policy of concentration-based standards.
- To make such proposals and recommendations as pertained to the consideration by IESAG of the above items for transmittal to the Illinois Pollution Control Board (IPCB) and the Illinois Environmental Protection Agency (IEPA).

The documentation upon which the IESAG based its considerations included References 5 and 6 of this report. In its report to the State of Illinois, IESAG concluded that for common pollutants treated by identical technologies, uniform concentration-based standards were desirable (8). Further, from its evaluation of the capabilities and limitations of that technology, IESAG recommended that the State of Illinois establish the effluent standards listed in Table 3. In essence, these recommendations represent BPT-equivalent limitations. The single exception to the BPT-equivalent basis of performance was for mercury. Recognizing the extreme environmental hazards of mercury, IESAG recommended the imposition of a mercury standard based upon best available technology, identified as ion exchange or coagulation treatment. Thus, the recommended mercury standard in Table 3 is BAT-equivalent. Technology associated with the other standards presented in Table 3 are,

Arsenic	Precipitation/Clarification
Barium	Precipitation/Clarification
Cadmium	Precipitation/Clarification
Chromium (hexavalent)	Chemical Reduction or Ion Exchange
Chromium (total)	Precipitation/Clarification
Copper	Precipitation/Clarification
Cyanide	Alkaline Chlorination
Fluoride	Lime Precipitation/ Clarification
Iron	Precipitation/Clarification
Lead	Precipitation/Clarification

Table 3. IESAG Standards for BPT-Equivalent Control Technology Proposed to the State of Illinois (8).

Pollutant		Concentration, mg/l	
		Thirty-Day Averaged	Maximum 24-Hour Composite
Arsenic	(total)	0.25	0.5
Barium	(total)	2.0	4.0
Cadmium	(total)	0.15	0.3
Chromium	(hexavalent)	0.1	0.2
Chromium	(total)	1.0	2.0
Copper	(total)	0.5	1.0
Cyanide	(total)	0.1	0.2
Fluoride	(total)	15.0	30.0
Iron	(total)	2.0	4.0
Lead	(total)	0.2	0.4
Mercury	(total)	0.003	0.006
Nickel	(total)	1.0	2.0
Silver	(total)	0.1	0.2
Zinc	(total)	1.0	2.0

Nickel	Precipitation/Clarification
Silver	Ion Exchange
Zinc	Precipitation/Clarification

Table 4 compares these IESAG recommended BPT-equivalent limitations with the range of BPT limitations proposed and promulgated by the USEPA.

Table 4. Expected Effluent Values for Application of Good Technology (30-day Average).

Pollutant	Type Treatment	IESAG Recommended Standards, mg/l	Range of BPT Values, mg/l
Arsenic	Coprecipitation	0.25	0.01-10.0
Cadmium	Precipitation	0.15	0.05- 0.5
Chromium(T)	Precipitation	1.0	0.05- 5.0
Copper	Precipitation	0.5	0.03- 1.1
Fluoride	Lime Precipitation	15.0	0.7 -29.0
Lead	Precipitation	0.2	0.1 - 2.1
Nickel	Precipitation	1.0	0.1 - 2.2
Zinc	Precipitation	1.0	0.1 - 5.0

In support of the development of BAT-equivalent control limitations for this report, the BPT-equivalent limitations recommended by IESAG (Table 3) have been reviewed. Technical performance data reported since the period of the IESAG study (7) has been considered in this review. There is no data available at this time to support revision of the IESAG recommendations as BPT-equivalent limitations.

Table 3 presents BPT-equivalent standards for 30-day average and 24-hour maximum discharge. The ratio of the two values

is 1:2. This ratio reflects the performance expected for well designed and properly operated wastewater treatment systems.

III. TREATMENT TECHNOLOGIES

This Chapter provides a brief synopsis of the most effective treatment technologies established in full-scale practice for each of the subject pollutants. Detailed discussions of these technologies have been published (4,5).

Arsenic. In aqueous systems, arsenic exists as either the arsenite ion (AsO_2^-; As^{+3}) or arsenate ion (AsO_4^{-3}; As^{+5}). Treatment methods for arsenic include lime or sulfide precipitation, or coprecipitation (sometimes described as precipitation/coagulation) with iron or aluminum hydroxide. The oxidation state of the arsenic influences the efficiency of each of these treatment processes. Sulfide precipitation is partially effective for arsenate, but ineffective for arsenite. Lime precipitation is preferred over sulfide precipitation due to higher treatment efficiency, but has the disadvantage of high required treatment pH (pH 12+). Caustic precipitation is less effective than lime. Iron or aluminum coprecipitation is more effective than is lime precipitation, but has the disadvantage of yielding greater quantities of sludge, which is often more difficult to dewater than is the lime precipitate sludge. Both iron and aluminum coprecipitation are strongly influenced by treatment pH, with aluminum treatment efficiency declining at pH above 7, and iron treatment efficiency declining above pH 9. Both processes perform better on arsenate than arsenite.

Thus, for all precipitation treatment processes for arsenic, enhanced performance is observed when the arsenic is present

as arsenate. Most effective treatment may require a chemical oxidation step, to convert any arsenite to arsenate. Chlorination has been used to achieve this oxidation. Each of the precipitation processes is, in addition, influenced by the efficiency of suspended solids removal. Clarification normally provides adequate solids removal, due to the quantities of lime, or iron or aluminum salts required for precipitation.

Barium. Barium is infrequently encountered in industrial wastewaters, and the treatment literature on barium is scant. Barium sulfate precipitation has been reported, with enhanced gravity clarification of the fine barium sulfate solids achieved upon addition of a coagulant such as an iron salt. Barium sulfate is relatively soluble, but addition of a salt such as sodium or iron sulfate in excess will reduce barium solubility and thereby improve treatment efficiency. When coagulants are employed, gravity clarification is effective for solids removal, and little gain in effluent quality is observed through filtration. The barium sulfate precipitation reaction appears to reach equilibrium rather slowly, and adequate reaction time in the treatment process is essential.

Cadmium. Precipitation is the principal treatment process employed for cadmium. Most effective precipitation treatment is achieved between pH 9 and 12, and close process control is required to promote maximum precipitation. In wastewaters of moderate to high carbonate, or to which supplemental carbonate has been added, the extremely insoluble cadmium carbonate is

formed, with best treatment near pH 10. Cadmium plating wastes typically contain cyanide, and pretreatment to completely destroy the cyanide is necessary for effective cadmium precipitation. Lime precipitation appears to yield a better settling precipitate than does caustic, and filtration of caustic treated wastes may be required to achieve an effluent quality comparable to that obtained with gravity clarification of a lime treated waste. Although it has been reported that ion exchange treatment yields effluent levels equal to or less than good precipitation treatment, there is inadequate full scale data in the technical literature to support this claim.

Hexavalent Chromium. Reduction of hexavalent chromium from a valence state of plus six to plus three, and subsequent hydroxide precipitation of the trivalent chromic ion, is the most common method of hexavalent chromium control. Some industries utilize ion exchange for chromic acid control and recovery. The standard reduction treatment technique is to lower the waste stream pH to 2.0-3.0 with sulfuric acid, and convert the hexavalent chromium to trivalent chromium with a chemical reducing agent such as sulfur dioxide, sodium bisulfite or ferrous sulfate. One common source of the latter is spent pickle liquor and, in the subsequent precipitation step the iron will function as a coagulant at the expense of about four-fold greater sludge production. The efficiency of conversion of the hexavalent to trivalent chromium is interdependent upon the allowed reaction time, treatment pH, and type and concentration

of reducing agent used. Close process control is necessary to achieve effective chromium reduction.

Ion exchange has been employed successfully for hexavalent chromium control. In the ion exchange system wastewater pH is a critical factor in successful treatment. At pH below 4, the oxidizing power of the chromic acid attacks the resin. At pH above 6, the ratio of dichromate to chromate increases. Since most anion exchange resins are less selective for dichromate than for chromate, ion exchange efficiency decreases.

Total Chromium. Total chromium is the sum of the hexavalent plus trivalent chromium. Where hexavalent chromium is a precurser form converted to trivalent chromium and the conversion has been ineffective, the total residual chromium may be predominately in the hexavalent form. Thus, in chromium control by reduction-precipitation, effective treatment requires the successful accomplishment of three sequential steps: hexavalent chromium reduction to trivalent chromium; precipitation of the trivalent chromium; and removal of the precipitated chromium. Treatment performance will deteriorate due to incomplete achievement at any one of these three stages.

Precipitation of trivalent chromium is most effective at pH 8.5-9.5 although, due to the presence of other metals with different pH optima in the typical metals-bearing wastewater, an average waste stream treatment pH of about 8 is often reported for mixed chromium-metals wastes. Lime and caustic are the pH control chemicals of choice, with caustic being most common in newer or upgraded treatment plants due to its ease

of handling. In the gravity clarification stage, lime treated wastes seem to settle better than do caustic treated wastes, and filtration of these latter wastes may be necessary to achieve suspended solids control equal to gravity clarification of the lime treated wastewater. Lime sludge may be two to three fold greater (dry weight basis) than a caustic sludge, for treatment of the same wastewater. Thus, in precipitation treatment while lime treatment may not necessitate filtration, the choice may be caustic treatment plus filtration, with the expense of the filter offset by greater ease of caustic handling, and reduced volumes of caustic sludge. These same trade-offs apply for precipitation treatment of many metals.

Copper. The standard treatment method for copper is precipitation. Cyanide, or moderate to high concentrations of carbonate will complex with copper, and prevent its precipitation. Although most authorities agree that optimum copper precipitation occurs between pH 9.0 and 10.3, effective treatment has been observed at much lower operating pH values. Poor performance in copper treatments seems more often to result from insufficient solids removal than from inadequate precipitation process pH control.

Both lime and caustic are widely used to precipitate copper. In copper sulfate wastewaters, the addition of lime may result in calcium sulfate formation. In this instance filtration should be avoided, since the slowly forming calcium sulfate will tend to cement the filter. With lime treatment, gravity clarification can provide as effective treatment as,

in contrast for some other metals, can caustic. The caustic sludge yield can be significantly less than that from lime treatment, although the caustic sludge dewatering properties are poorer than are the lime sludges. In summary, effective copper precipitation treatment can be achieved over a fairly wide pH range, and close pH control is thus not critical. Gravity clarification is effective in solids removal, and little or no benefit is gained by effluent filtration. The result is that BAT-equivalent control is comparable to BPT-equivalent control, being based upon the same wastewater treatment technology.

Cyanide. Cyanide treatment results reported for full-scale systems are among the most erratic observed for any inorganic industrial pollutant. This is primarily due to the variety of complexes which form with cyanide within different wastewaters, and the extent to which these cyanide complexes differ in their response to the standard cyanide destruction techniques. These differences are reflected in the higher effluent limitations normally promulgated for total cyanide than for cyanide amenable to chlorination treatment.

Several methods of treating cyanide wastes are in current use, although the most wide-spread is alkaline chlorination. Most effective alkaline chlorination is through two-stage treatment. The first stage is designed and operated to maximize conversion of cyanide to cyanate, which is destroyed by additional chlorination in the second stage. There are reports

that equivalent treatment can be achieved in a single stage process, although some results suggest that the single stage approach suffers from a lack of process stability. Close process control, and automated pH and chlorine dosage are necessary to accomplish a high degree of cyanide treatment. In the first stage, a pH of 10 or higher, and a reaction period of up to two hours is necessary. To avoid formation of solid cyanide precipitate, the waste must be thoroughly agitated during treatment. In the second stage, an operating pH of 8.0-8.5 and reaction period of up to one hour is necessary, with sufficient chlorine addition to force cyanate oxidation.

Other cyanide treatment processes include ozone oxidation and electrolytic decomposition. The former has had limited field application and the latter process is used primarily for concentrated cyanide baths, with residual treatment by alkaline chlorination.

Fluoride. Treatment options for fluoride are limited to two alternative precipitation processes, with significant differences in performance and associated sludge yield. Lime precipitation to form calcium fluoride has been the dominant technology for fluoride control. At the high treatment pH required (pH 12+), and associated high lime dosage filtration is risky, due to the tendency of the gravity clarified effluent to cement the filter. Thus, within the solubility constraints associated with calcium fluoride formation, most effective treatment with lime depends upon highly efficient solids removal by gravity clarification. The precipitated solids are reported

to have poor settling characteristics. This lime precipitation/clarification technology provided the basis for BPT effluent limitation guidelines.

The second treatment alternative is fluoride removal by alum addition; essentially a coprecipitation process. Much lower effluent fluoride levels are achieved with alum coprecipitation than with lime precipitation and best removal appears to result at pH 6-7. Treatment efficiency in this pH range reflects the alum dosage (mg/mg fluoride), with enhanced treatment at higher (200+ mg/mg) alum dosages. A major disadvantage of the process is the voluminous sludge produced, which even at moderate alum dosages can represent up to 40% of the original wastewater volume treated. This sludge yield represents such a serious problem that lime precipitation has remained the treatment technology of choice of both regulatory agencies and industry.

Iron. In aqueous systems, iron exists in the ferric (Fe^{+3}) or ferrous (Fe^{+2}) form, depending upon conditions of pH and dissolved oxygen concentration. In precipitation treatment, ferrous iron is more soluble than ferric iron. Therefore, most effective iron precipitation treatment incorporates conversion of any ferrous to ferric iron, before precipitation. At neutral pH and in the presence of oxygen, ferrous iron rapidly oxidizes to the ferric form, which readily hydrolyzes to the insoluble precipitate, ferric hydroxide. Many iron wastewaters such as pickling rinses are both highly acidic and contain predominately the ferrous form of iron.

The principal treatment process for iron is oxidation-precipitation-clarification. The iron wastewater is first neutralized to pH near 7, where ferrous iron oxidation rapidly occurs and where the solubility of ferric hydroxide is at its minimum. Following or simultaneous with pH adjustment, the waste is aerated to provide oxygen for the iron oxidation process. Where iron complexing agents are present in the waste, the rate of oxidation is slowed. Sufficient aeration time is therefore essential in order to achieve a high degree of oxidation. Freshly precipitated ferric hydroxide has a characteristic low specific gravity, which makes settling difficult without long clarifier detention time or additional treatment such as filtration. Lime is frequently used for pH adjustment and, where sulfuric acid is present as in a pickling waste, large quantities of calcium sulfate are also precipitated. In some industrial wastes, ferrous and ferric iron may exist in the presence of cyanide. Extremely stable iron cyanide complexes result. Such species present considerable difficulties for both iron and cyanide treatment. No truly effective treatment method has been reported for such wastes.

Lead. Precipitation treatment of lead is extremely effective, except in instances such as the tetraethyl lead industry where significant concentrations of organic lead occur. Lead in the organic form is not amenable to precipitation, and the organic component must be destroyed by chemical means such as chlorination, before the lead can be precipitated. Although

the literature contains conflicting values of pH options for lead precipitation (ranging from pH 6 to above pH 10), there is strong evidence that best precipitation treatment occurs in the pH range 9-10. At this high treatment pH, other metals in the wastewater with lower pH optima may not be effectively precipitated, however. Lead wastewaters precipitated with lime have good settling properties, while caustic treated wastes may require filtration to achieve an equivalent effluent lead level. The expense of caustic plus filtration may be offset by the lesser sludge volumes produced with caustic treatment.

Mercury. Many types of mercury treatment technology have been described in the technical literature. Among the most effective are the ion exchange and coagulation treatment processes. Typically, ion exchange treatment of mercury involves the formation of a negatively charged mercuric chloride complex by addition of chlorine or hypochlorite (to oxidize any metallic mercury present), or chloride salts, and removal of the mercuric chloride complex or an anion exchange resin. Most experience with ion exchange treatment has been with chlor-alkali wastes which contain high background chloride levels.

Control of mercury by coagulation has been reported for a variety of mercury-containing wastewaters. The process has been applied with success to both organic and inorganic mercury. Iron and alum coagulants are reported to produce equivalent mercury removal results, although the alum coagulant may display poorer settling properties than the iron coagulant. In both instances effluent filtration is necessary to achieve best

treatment results. A disadvantage of coagulation treatment is that large quantities of mercury-contaminated iron or aluminum hydroxide sludge are produced.

Because of the large sludge quantities generated, activated carbon adsorption is sometimes considered as an alternative to coagulation. However, carbon adsorption is less effective than ion exchange or coagulation at higher influent mercury levels, and it appears that carbon treatment yields effluent mercury levels comparable to ion exchange or coagulation only when initial mercury levels are below 50 µg/l.

Nickel. In waste streams, nickel exists predominately as the soluble ion. In the presence of complexing agents such as ammonia, EDTA, or cyanide, nickel can form extremely stable soluble complexed species which interfere with conventional precipitation treatment.

Precipitation treatment is the standard practice for control of nickel in industrial wastes, although in specialized circumstances such as for recovery in plating plants, reverse osmosis has been utilized. This later technology, although effective, is principally utilized for alkaline nickel wastes. Best precipitation treatment is achieved at a pH above 9.5, which pH level may cause deterioration of the precipitation treatment of other metals in the wastewater having significantly lower pH options. Even when lime is employed as the treatment chemical, nickel hydroxide precipitates have rather poor settling characteristics. Poor performance in nickel treatment more often results through inadequate solids separation than

through incomplete precipitation of the soluble nickel. Unless extended clarifier detention time is provided, filtration appears necessary to achieve good control of total nickel.

Silver. Treatment technology for silver is influenced more by the value of the recovered metal than by the limitations of discharge permits. Many treatment/recovery techniques are employed, although the final polishing step is often ion exchange. Other processes include evaporation recovery, coprecipitation with ferric chloride, and silver chloride precipitation. This latter process is least efficient. Coprecipitation and ion exchange yield comparable results, and evaporative treatment results in complete recovery. Evaporation is rarely economical for dilute silver wastewaters.

Zinc. Precipitation is the standard of practice in treatment of zinc wastewaters. There is a great deal of confusion in the technical literature regarding the optimum pH for zinc precipitation. Optimum performance has been cited at pH values as low as 9.0 to 9.5, and as high as pH 11 and above. Zince is an amphoteric metal, with increasing solubility at both higher and lower pH. It is possible that constituents (such as complexing agents) other than zinc in the various wastewaters may influence zinc precipitation efficiency as a function of pH. As with other metal wastewaters, both lime and caustic are used as the precipitating chemical. The effluent quality of full-scale zinc treatment systems appears to be influenced most by the efficiency of precipitate suspended solids removal and many such systems employing only gravity clarification for solids

control exhibit high effluent solids and associated high effluent zinc. Therefore, for zinc wastes, best available technology requires determination of and treatment at the best pH value for that specific wastewater, plus efficient suspended solids removal by gravity clarification and/or filtration.

IV. BAT-EQUIVALENT CONTROL

Under the authority of the Clean Water Act of 1977, the USEPA is developing BAT effluent limitations guidelines for industrial point source dischargers. Guidelines for only a few industrial categories have been published to date. Example guidelines are presented in Table 5. As was the case for BPT guidelines, a range of concentration values is observed for each pollutant regulated. The range of guidelines for copper is most extreme, at 200-fold.

Table 6 compares BPT guidelines for several pollutants with the BAT values listed in Table 5, for three industry categories. Although it might be expected that BAT performance should be equal to or more restrictive than BPT, such is not consistently the case, (see total chromium, fluoride). For several of the cases presented in Table 6, BPT and BAT values are equal. For most instances where BAT is below BPT, the reduction is fairly modest. The exception in Table 6 is nickel, with a BPT guideline of 2.20 mg/l versus a BAT guideline of 0.10 mg/l.

On the basis of the BAT information available to date, it appears that a pattern of varying concentration based values will result through the USEPA efforts. This Chapter of this report presents single BAT-equivalent values for each subject pollutant, developed through a technology performance evaluation. These BAT-equivalent effluent values are summarized in Table 7, for 30-day average performance. Based upon performance data of full-scale systems, a 24-hour maximum discharge value of 1.5 to 2.0 times the 30-day average (Table 7) is recommended.

Table 5. Example Proposed and Promulgated BATEA Effluent Limitation Guidelines - Thirty-Day Average.

Industry Category	Document	As	Cd	Cr-H	Cr-T	Cu	CN	F	Fe	Pb	Hg	Ni	Ag	Zn
Inorganic Chemicals[b]	440/1-79/007													
Chlor-Alkali Mercury Cells		0.10	0.05			0.05				0.16	0.048	0.10	0.07	0.15
Chlor-Alkali Daiphragm Cells					0.05	0.40				0.22		0.10		0.40
Hydrofluoric Acid					0.04	0.009		33		0.06		0.15		0.52
Sodium Dichromate				0.05	0.32							0.17		0.47
Titanium Dioxide-Sulfate Process		0.50	0.15		0.14	0.50			2.50	0.30		0.20		0.50
Titanium Dioxide-Chloride Process					0.14				2.40					
Titanium Dioxide-Chloride Ilmenite Process		0.50	0.10		0.10	0.50			2.50	0.30		0.20		0.50
Aluminum Fluoride					0.04			30				0.17		
Chrome Pigments			0.19		1.10	0.40				1.40		0.17		1.10
Copper Sulfate		0.50	0.05		0.05	0.40				0.05		0.10		0.40
Hydrogen Cyanide														
Free							0.27							
Total							4.00							
Nickel Sulfate					0.05	0.40				0.05		0.20		0.40
Sodium Hydrosulfite					0.10					0.30		0.20		0.50
Sodium Bisulfite					0.11		0.50			0.30		0.20		0.50

Table 5. (Continued).

Industry Category	Document	As	Cd	Cr-H	Cr-T	Cu	CN	F	Fe	Pb	Hg	Ni	Ag	Zn
Textile Mills (all subcategories)	440/1-79/022b				0.50	0.50								1.00
Gum & Wood Chemicals Rosin Based Derivatives	440/1-79/078b													1.80
Sulfate Turpentine						1.80						1.80		
Leather Tanning & Finishing	440/1-79/016				1.80									
Steam Electric Power	440/1-80/029b					1.00			1.00					
Pulp, Paper & Paperboard[a]														3.00
Range - Minimum		0.10	0.05	0.05	0.04	0.009	0.50	30	1.00	0.05	0.048	0.10	0.07	0.15
- Maximum		0.50	0.19		1.80	1.80	4.00	33	2.50	1.40		1.80		3.00
Median Value		0.50	0.10	-	0.10	0.40	-	-	2.50	0.30	-	0.17	-	0.50

[a] Daily maximum values reported. No standards proposed for 30-day consecutive average performance.

[b] BAT and PSES mass discharge limitations are equal. PSES limitations were proposed on both a concentration and a mass discharge basis. The PSES limitation values are presented in this Table.

Table 6. Comparison of Selected BPT and BAT Effluent Limitations Guidelines - Thirty-Day Average.

Pollutant	Industry Category	Subcategory	BPT(Ref.6)	BAT(Tab. _)
Chromium(Hexavalent)	Inorganic Chemicals	Sodium Dichromate	0.05	0.05
Chromium(Total)	Inorganic Chemicals	Chrome Pigments	0.50	1.10
		Sodium Dichromate	0.44	0.32
	Leather Tanning & Finishing	-	1.00-3.60	1.80
Copper	Inorganic Chemicals	Copper Sulfate	1.10	0.40
	Steam Electric Power	Metal Cleaning	1.00	1.00
Fluoride	Inorganic Chemicals	Alumimum Fluoride	20.0	30.0
		Hydrofluoric Acid	15.0	33.0
Iron	Inorganic Chemicals	Titanium Dioxide	4.00	2.50
	Steam Electric Power	Metal Cleaning	1.00	1.00
Lead	Inorganic Chemicals	Chrome Pigments	2.10	1.40
Nickel	Inorganic Chemicals	Copper Sulfate	2.20	0.10
Zinc	Inorganic Chemicals	Chrome Pigments	4.00	1.10

Table 7. Summary of BAT-Equivalent Treatment Technologies and Effluent Pollutant Levels Achievable on a Thirty-Day Averaged Basis.

Pollutant	BAT-Equivalent Concentration, mg/l	Treatment Technology
Arsenic	0.20	Arsenite Oxidation; Lime Precipitation, or Iron or Alum Co-Precipitation; Gravity Clarification
Barium	1.00	Sulfate Precipitation; Coagulation; Gravity Clarification
Cadmium	0.10	High pH Precipitation; Gravity Clarification, or Filtration Where Caustic is Substituted For Lime
Chromium, Hexavalent	0.05	Acidic Reduction To Trivalent Chromium or Ion Exchange at pH Below 6.0
Chromium, Total	0.50	Precipitation; Gravity Clarification, except Filtration may be Required for Caustic Treated Wastewaters
Copper	0.40	Precipitation; Gravity Clarification
Cyanide	0.10	Two-Stage Alkaline Chlorination
Fluoride	10.0	High pH Lime Precipitation; Gravity Clarification
Iron	1.50	Oxidation at Neutral pH of Ferrous to Ferric Iron; Precipitation; Gravity Clarification or Filtration

Table 7. (Continued).

Pollutant	BAT-Equivalent Concentration, mg/l	Treatment Technology
Lead	0.15	High pH Precipitation; Gravity Clarification, or Filtration where Caustic is Substituted for Lime
Mercury	0.003	Ion Exchange or Coagulation plus Filtration
Nickel	0.75	High pH Precipitation; Gravity Clarification and/or Filtration
Silver	0.10	Ion Exchange or FErric Chloride Coprecipitation plus Filtration
Zinc	0.50	Optimized Precipitation pH; Gravity Clarification and/or Filtration

BAT-equivalent effluent quality requires both in-plant water conservation, and maximum efficiency of operation of well designed and properly constructed and maintained treatment systems. In some instances, for precipitated solids removal, clarification alone can yield an effluent quality equal to final effluent filtration. However, these are rather rare instances, and filtration would normally be required to achieve the BAT-equivalent effluent pollutant levels cited in this Chapter. An advantage of filtration is that it normally provides more consistent effluent quality than does clarification alone, since clarifiers are prone to upset.

Arsenic. BAT-equivalent treatment technology for arsenic can be achieved by oxidative conversion of arsenite to arsenate, followed by either lime precipitation at pH 12 or iron coprecipitation at pH below 9, and gravity clarification. In a well designed and properly operated treatment system, an effluent arsenic level of 0.20 mg/l is obtainable. Filtration would provide only marginal enhancement of the effluent quality.

Barium. Sulfate precipitation of barium is the only well established treatment technology available. BAT-equivalent treatment requires sufficient detention time to achieve equilibrium formation of the barium sulfate solids, and the use of a coagulant such as iron or aluminum sulfate to control suspended solids removal by gravity clarification. A BAT-equivalent barium effluent quality of 1.0 mg/l is achievable.

Cadmium. BAT-equivalent control of cadmium results through complete destruction of cyanide where present, followed by lime precipitation plus gravity clarification or caustic precipitation plus filtration. In a closely controlled treatment plant with highly efficient solids removal, an effluent cadmium level of 0.10 mg/l is achievable.

Hexavalent Chromium. Chemical reduction of hexavalent to trivalent chromium followed by precipitation of the trivalent chromic hydroxide is a well established technology. The process, with adequate reaction time, and close process control of pH and reducing agent dosage, can achieve a BAT-equivalent hexavalent chromium concentration of 0.05 mg/l. Ion exchange treatment, when wastewater pH is controlled to minimize formation of dichromate, can achieve an effluent hexavalent chromium concentration equal to the chemical reduction process.

Total Chromium. BAT-equivalent control for total chromium will yield an effluent chromium level of 0.5 mg/l. This treatment is precipitation and clarification. Where caustic is used as the treatment chemical, effluent filtration may be required to achieve the cited concentration.

Copper. Treatment by precipitation and gravity clarification will yield BAT-equivalent control of copper to an effluent level of 0.4 mg/l. Although close process pH control does not appear to be critical, effective solids separation is necessary to achieve this effluent quality.

Cyanide. Alkaline chlorination treatment represents BAT-equivalent control of cyanide, and in the absence of extremely strong metal-cyanide complexes, can achieve an effluent cyanide concentration of 0.10 mg/l. In recognition of the differences in chemical forms and their associated treatability of cyanide in different process streams, cyanide treatment must often be evaluated for individual dischargers where BAT-equivalent control technology cannot achieve 0.1 mg/l.

Fluoride. Lime precipitation plus gravity clarification represents BAT-equivalent control technology for fluoride. Effective treatment requires high treatment pH and lime dosage, as well as efficient solids removal, and can achieve an effluent fluoride concentration of 10 mg/l.

Iron. BAT-equivalent control of iron requires efficient oxidation of ferrous to ferric iron, followed by precipitation and solids removal. In most instances, solids removal by gravity clarification will yield an effluent iron concentration of 1.5 mg/l. Rarely, filtration may be required in order to achieve this effluent quality.

Lead. Effective treatment of lead requires precipitation at pH near 10, plus effective suspended solids removal. Where lime is employed as the treatment chemical and adequate clarifier detention time is provided, an effluent lead level of 0.15 mg/l is achievable. With caustic used in lieu of lime, a poorer settling precipitate results and filtration may be necessary to achieve an effluent lead concentration of 0.15 mg/l.

Mercury. BAT-equivalent control of mercury can be achieved by ion exchange treatment, or by coagulation with effluent filtration. At raw wastewater mercury levels below about 50 µg/l, activated carbon adsorption will perform equivalent to the other two processes. An effluent mercury level of 3 µg/l is achievable in well designed and properly operated treatment systems.

Nickel. Precipitation treatment of nickel is effective in converting the soluble ion to a solid nickel hydroxide phase. However, the precipitate appears to have poor settling characteristics and effective solids removal is accomplished only with either long clarifier detention time or by filtration. Either approach can achieve an effluent nickel level of 0.75 mg/l.

Silver. BAT-equivalent control of silver can be accomplished by either ion exchange or ferric chloride coprecipitation treatment. Either method will yield an effluent silver level of 0.10 mg/l. With coprecipitation, effluent filtration may be required to achieve this effluent silver level.

Zinc. The efficiency of precipitation treatment for zinc is influenced by the treatment pH (with the optimum pH value apparently varying among different wastewaters) and efficient suspended solids removal. A BAT-equivalent effluent zinc level of 0.5 mg/l is achievable when these conditions are met.

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